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(21) International Application Number: PCT/US99/09430 (22) International Filing Date: 29 April 1999 (29.04.99) (30) Priority Data: <table border="0"><tr><td>09/103,386</td><td>24 June 1998 (24.06.98)</td><td>US</td></tr><tr><td>09/103,856</td><td>24 June 1998 (24.06.98)</td><td>US</td></tr><tr><td>09/104,309</td><td>24 June 1998 (24.06.98)</td><td>US</td></tr></table> (71) Applicant: ISP INVESTMENTS INC. [US/US]; 818 Washington Street, Wilmington, DE 19801 (US). (72) Inventors: ULMER, Herbert, W.; 714 Washington Street, Hoboken, NJ 07030 (US). GILLECE, Timothy; 5516 Tudor Drive, Pompton Plains, NJ 07444 (US). KATIRGIS, John, A.; 123 Runnymede Road, West Caldwell, NJ 07006 (US). FOLTIS, Linda, C.; 16 Highfield Lane, Nutley, NJ 07110 (US). BLAINE, April; 11 Muscotah Road, Highland Lakes, NJ 07422 (US). (74) Agents: MAUE, Marilyn, J. et al.; International Specialty Products, Legal Dept., Building 10, 1361 Alps Road, Wayne, NJ 07470 (US).		09/103,386	24 June 1998 (24.06.98)	US	09/103,856	24 June 1998 (24.06.98)	US	09/104,309	24 June 1998 (24.06.98)	US	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
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(54) Title: DERIVATIZED POLYMERS OF α -OLEFIN-MALEIC ANHYDRIDE ALKYL HALF-ESTER OR FULL ACID (57) Abstract <p>What is described herein are derivatized polymers of α-olefin-maleic anhydride alkyl half-ester or full acid, preferably the isobutylene compound, optionally with repeat units of maleamic acid and/or its corresponding maleimide therein. These polymers are useful as fixatives in personal care products, such as hair spray compositions, particularly as one-phase, low VOC formulations in pump and aerosol systems, and in anhydrous, alcoholic, aqueous-alcoholic and in high hydrocarbon tolerant solvent formulations. In use, these hair spray compositions dry down to form clear, continuous and defectless films.</p>											

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DERIVATIZED POLYMERS OF α -OLEFIN-MALEIC
ANHYDRIDE ALKYL HALF-ESTER OR FULL ACID

BACKGROUND OF THE INVENTION

This invention relates to polymers of maleic anhydride, and, more particularly, to polymers of α -olefin-maleic anhydride alkyl half-ester or full acid, optionally with repeat units of maleamic acid and/or its maleimide, and to hair spray compositions which include these polymers as fixatives.

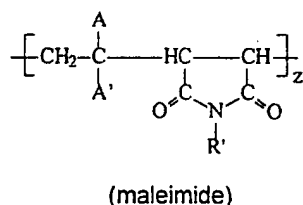
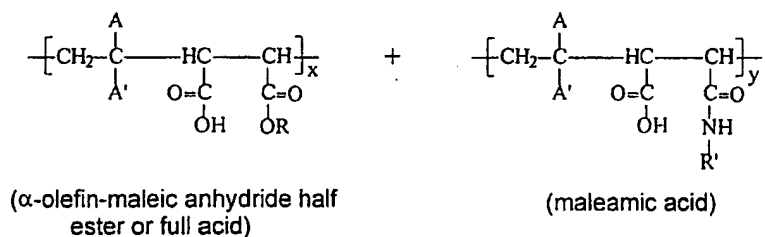
Hair spray compositions usually contain film-forming polymers as fixatives in a suitable delivery system. Particularly desirable are polymers which can be formulated as one-phase hair spray compositions and which dry down to form continuous, clear and defectless films.

SUMMARY OF THE INVENTION

What is described herein are polymers of α -olefin-maleic anhydride alkyl half-ester or full acid, optionally with repeat units of maleamic acid and/or its corresponding maleimide therein. These polymers are particularly useful as fixatives in hair spray compositions, particularly as one-phase, 55-80% VOC formulations in both pump and aerosol applications, in anhydrous or aqueous-alcoholic formulations, and in high hydrocarbon tolerant formulations. In use, these compositions dry down to form continuous, clear and defectless films.

DETAILED DESCRIPTION OF THE INVENTION

The polymers of the invention contain repeat units of an α -olefin-maleic anhydride alkyl half-ester or full acid, optionally with repeat units of maleamic acid and/or maleimide. Their general formula is given below:

FORMULA I

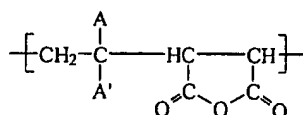
where A and A' are independently H or C₁-C₄ alkyl;

R is H or C₁-C₄ alkyl and R' is an α -unsubstituted primary amine or hydroxy-containing α -unsubstituted primary amine having one or more of the following groups therein; hydrogen, silyl, amino, olefinic, carboxy and halogen; and

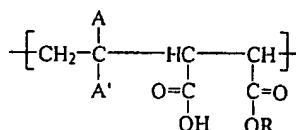
x is 0.01-1; y is 0-0.95; and z is 0-0.99.

The derivatized polymers of the invention are made by reacting an α -olefin-maleic anhydride copolymer or α -olefin-maleic anhydride alkyl half-ester copolymer, having the formula:

FORMULA II



α -olefin-maleic anhydride
copolymer



α -olefin-maleic anhydride alkyl
half-ester or full acid copolymer

in an aqueous, alcohol or aqueous-alcoholic solution, ROH, where R is as defined above, with an α -unsubstituted primary amine, RNH₂, such as n-hexylamine, n-octylamine or 2-ethylhexylamine, or hydroxy-containing α -unsubstituted primary amine. Ammonia, or a silylated primary amine, fluorinated primary amine, halogenated primary amine, unsaturated amine, cyanoamine, alcohol amines and amphoteric amines, also may be used. The reaction is carried out at a reaction temperature of about 80-150°C, preferably about 100-130°C, for about 1-25 hours, preferably 2-10 hours.

In one embodiment of the invention, a polymer having no amide repeat unit, i.e. all amide has been converted to the cyclic imide form, can be obtained by carrying out the process at 115°C. for 5 hours or longer. The resultant polymer thus includes only half-ester and cyclic imide repeat units therein.

Higher reaction temperatures and longer reaction times enhance the conversion of amide into the corresponding cyclic imide repeating unit by loss of a water molecule.

The α -olefin-maleic anhydride or α -olefin-maleic anhydride alkyl half-ester copolymers used as starting materials in the process of the invention are made by a suspension polymerization method in a hydrocarbon solvent. In this method, the suspending agent and a free radical polymerization initiator are charged to a reactor and purged with nitrogen gas. Then the reactor is heated to 60°C and a predetermined amount of molten maleic anhydride is introduced into the reactor vessel. Then the reactor is heated to 80°C and isobutylene is fed in continuously over a predetermined amount of time. The resultant feed rate is based on the efficiency of removal of heat from the system which is evolved during the polymerization reaction. Upon completion of the reaction, a white suspension of the polymer in the solvent is obtained which can be dried to provide a free-flowing, white powder of the desired copolymer.

Alternatively, the suspension can be pumped into a reactor and sparged with heated ethanol or water to remove the lower boiling hydrocarbon solvent and effect conversion of the anhydride polymer to its corresponding ethyl half-ester or diacid derivative.

Preferably the suspension polymerization is carried out under these conditions:

(a) the reactant solids are maintained at about 20 to 50%, preferably about 30%;

(b) the suspending agent is a hydrocarbon soluble resin, preferably containing maleic anhydride, e.g. p(octadecylvinylether-co-maleic anhydride) or p(octadecylene-co-maleic anhydride);

(c) the suspending agent is present in an amount of about 0.25 to 3 wt. % solids;

(d) the isobutylene reactant is fed into molten maleic anhydride over a period of about 2 to 6 hours, most preferably about 4 hours;

(e) the initiator is an azo or peroxide initiator, with a half-life of at least 10 hours at a reaction temperature between about 60° and 90°C, preferably, a peroxide initiator;

(f) the reaction temperature is at least 80°C; and

(g) the hydrocarbon solvent is pentane or hexane.

Alternatively, the starting polymers of FORMULA I may be made by precipitation polymerization in a solvent such as isopropyl acetate.

HAIR SPRAY COMPOSITIONS

During drying, hair spray compositions containing polymers of the invention derivatized with long chain amines form films which go through a gel-like state upon further drying. The resultant film is a continuous, clear, defectless film.

The invention will now be illustrated by the following examples.

1. Preparation of Starting Materials

EXAMPLE 1

To a 2-liter, high pressure reactor was added: 98.06 g maleic anhydride monomer, 2.94 g decanoylperoxide initiator, 3.85 g octadecylvinylether as suspending agent and 240 g of pentane as solvent. Then the reactor was sealed and purged 3 times with nitrogen gas. The reactor was heated to 80°C over a 30 minute period. Upon reaching 80°C, 141.64 ml of isobutylene monomer was fed into the reactor over a 4-hour period. The reaction was continued for another 1 hour at 80°C and then cooled and discharged. The resultant product was a finely divided, off-white slurry of poly(isobutylene-maleic anhydride) copolymer in pentane.

2. Preparation of Copolymers of Formula I

EXAMPLE 2

Into a high pressure reactor was added: 75.4 g (0.490 mole) P(isobutylene-MAn) powder, 19.8 g octadecylamine (0.0735 mole) and 222.1 g ethanol. The reaction mixture was then purged with N₂ gas and the temperature was raised to 50°C and held there for 1 hour. Then the temperature was increased to 75°C, held for 2 hours, and thereafter to 100°C for 3 hours. Upon cooling the resultant product had a slightly green color and a slight haze. The dried polymer had an acid of 225 mg KOH/g polymer and contained about 2 wt. % free amine.

EXAMPLE 3Copolymer of Formula I

In a high pressure reactor was added:

60.86 g (0.395 mole) p(isobutylene-MAn) powder,
15.90 g (0.0590 mole) n-octadecylamine,
4.32 g (0.0590 mole) n-butylamine, and
270.3 g ethanol.

The resultant reaction slurry was stirred, sealed and purged with N₂ gas. The temperature was raised to and kept at 75°C for 2 hours and then raised to and kept at 100°C for 5 hours. Upon cooling, the reaction product was a clear slightly yellow solution. The resultant polymer had an Acid No. of 202 mg KOH/g polymer and 0.142 meq. free amine/g of product.

EXAMPLE 4

In a high pressure reactor was added:

65 g (0.422 mole) p(isobutylene-MAn) powder,
11.4 g (0.0423 mole) octadecylamine,
10.9 g (0.0843 mole) octylamine, and
204 g ethanol.

The resultant slurry was stirred, sealed and purged with N₂ gas. The temperature was raised to and kept at 75°C for 2 hours and then raised to and kept at 100°C for 5 hours. Upon cooling, the reaction product was a clear slight yellow solution. The resultant polymer had an Acid No. of 198 mg KOH/g polymer and 0.146 meq. free amine/g product.

EXAMPLE 5

To a 2-liter, high pressure reactor was added: 60.0 g (0.390 mole) p(isobutylene-maleic anhydride), 8.54 g (0.117 mole) n-butylamine, 10.82 g dodecylamine, 15.73 g (0.0584 mole) octadecylamine and 285 g ethanol. The reactor was purged with N₂ gas. The reactor was heated to 75°C and held for 2 hours and then heated to 100°C and held for 5 hours. The resultant material possessed an acid number of 146 mg KOH/g polymer.

EXAMPLE 6

To a 2-liter, high pressure reactor was added: 66.1 g (0.429 mole) p(isobutylene-maleic anhydride), 10.96 g (0.150 mole) n-butylamine, 11.90 g (0.0642 mole) dodecylamine, 5.77 g (0.0214 mole) octadecylamine and 285 g ethanol. The reactor was purged with N₂ gas. The reactor was heated to 75°C and held for 2 hours and then heated to 100°C and held for 5 hours. The resultant material possessed an acid number of 160 mg KOH/g polymer.

EXAMPLE 7

To a 2-liter, high pressure reactor was added: 64.7 g (0.420 mole) p(isobutylene-maleic anhydride), 8.14 g (0.0630 mole) 2-ethylhexylamine and 16.97 g (0.0630 mole) octadecylamine and 200 g ethanol. The reactor was purged with N₂ gas. The reactor was heated to 75°C and held for 2 hours and then heated to 100°C and held for 5 hours. The resultant material possessed an acid number of 205 mg KOH/g polymer.

EXAMPLE 8

To a 2-liter, high pressure reactor was added: 73.4 g (0.477 mole) p(isobutylene-maleic anhydride), 10.45 g (0.143 mole) n-butylamine and 12.83 g (0.0476 mole) octadecylamine and 171 g ethanol. The reactor was purged with N₂ gas. The reactor was heated to 75°C and held for 2 hours and then heated to 100°C and held for 5 hours. The resultant material possessed an acid number of 195 mg KOH/g polymer.

EXAMPLE 9

To a 2-liter, high pressure reactor was added: 66.0 g p(isobutylene-maleic anhydride and 198 g ethanol. The reactor was purged with N₂ gas. The reactor was heated to 130°C and held for 8 hours. The resultant material possessed an acid number of 265 mg KOH/g polymer.

EXAMPLE 10

To a 2-liter, high pressure reactor was added: 66.0 g (0.429 mole) p(isobutylene-maleic anhydride, 5.80 g (0.129 mole) ethylamine, 9.40 g (0.129 mole) n-butylamine and 198 g ethanol. The reactor was purged with N₂ gas. The reactor was heated to 100°C and held for 3 hours and then the reactor was heated to 130°C and held for 5 hours. The resultant material possessed an acid number of 120 mg KOH/g polymer.

EXAMPLE 11

Into a high pressure reactor was added:
22.8 g (0.148 mole) p(IB-MAn), 3.33 g ethylamine (0.0517 mole) (70%), 2.96 g water and 45.62 g ethanol. The reaction was purged with N₂ gas and the temperature raised to 100°C over 1 hour. Upon reaching 100°C, 5.44 g (0.0891 mole) ethanolamine dissolved in 19.85 g water was added to the reaction mixture. The reaction was held at 100°C for 1 hour and then raised to 130°C over 1 hour and held for an additional 8 hours. Cooling provided a clear yellow solution. The dried polymer had an acid number of only about 25 mg KOH/g polymer, indicating substantially all maleimide repeat units in the polymer.

EXAMPLE 12

Into a high pressure reactor was added:
154.0 g (1.00 mole) p(IB-MAn), 9.02 g ((0.140 mole) ethylamine (70%), 10.97 g (0.150 mole) butylamine and 316 g ethanol. The reaction was purged with N₂ gas and the temperature raised to 130°C over 2 hours and held for 3 hours. The reaction mixture was cooled to which was added 36.65 g (0.600 mole) of ethanolamine dissolved in 176 g of water. The reactor was gradually reheated to 130°C over 3 hours and held for 8 hours. A clear yellow solution provided a polymer having an acid number of about 65 mg KOH/g polymer.

EXAMPLE 13

Into a high pressure reactor was added: 60.0 g (0.390 mole) p(IB-MAn) powder (acid # 280 in ethanol), 14.5 g (0.198 mole) n-butylamine and 175 g ethanol. The reaction was purged with N₂ gas and the temperature raised to 130°C over 3 hours and held for 5 hours to provide the p(IB-MAn) half acid/ester. The reaction mixture then was cooled to 30°C and 11.9 g (0.195 mole) of ethanolamine dissolved in 25 g water was added slowly to the reaction mixture. The reactor was gradually reheated to 130°C over 3 hours and held for 5 hours. Upon cooling, a clear yellow solution was obtained. The dried polymer had an acid number of only about 35 mg KOH/g polymer. The reduced acid number indicating the predominance of the maleimide repeat unit therein over the maleamic acid unit.

EXAMPLE 14

Into a high pressure reactor was added: 154.0 g (1.00 mole) p(IB-MAn) and 326 g ethanol. The reaction was purged with N₂ gas and the temperature raised to 130°C over 2 hours and held for 3 hours. The reaction mixture was cooled to which was added 28.5 g (0.379 mole) 3-amino-1-propanol and 34.82 g (0.570 mole) of ethanolamine dissolved in 181 g water. The reactor was gradually reheated to 130°C over 3 hours and held for 8 hours. Upon cooling, a clear yellow solution was obtained. The dried polymer had an acid number of about 125 mg KOH/g polymer, indicating the presence of both maleamic acid and maleimide repeat units in the polymer.

EXAMPLE 15

Into a high pressure reactor was added: 154.0 g (1.00 mole) p(IB-MAN) and 320 g ethanol. The reaction was purged with N₂ gas and the temperature raised to 130°C over 2 hours and held for 3 hours. The reaction mixture was cooled to which was added 7.51 g (0.100 mole) 3-amino-1-propanol and 51.92 g (0.850 mole) of ethanolamine dissolved in 178 g of water. The reactor was gradually reheated to 130°C over 3 hours and held for 8 hours. The resultant product was a clear yellow solution. The dried polymer had an acid number of about 75 mg KOH/g polymer.

EXAMPLE 16

Into a high pressure reactor was added: 123 g (0.615 mole) monoethyl half ester of p(IB-MAN), 35.6 g (0.583 mole) ethanolamine, 88 g water and 199 g ethanol. The reaction was purged with N₂ gas and the temperature raised to 130°C over 2 hours and held for 8 hours. The resultant product was a clear yellow solution. The dried polymer had an acid number of about 70 mg KOH/g polymer.

EXAMPLE 17

Into a high pressure reactor was added: 22.8 g (0.148 mole) p(IB-MAN), 3.33 g ethylamine (0.0517 mole) (70%), 2.96 g water and 45.62 g ethanol. The reaction was purged with N₂ gas and the temperature raised to 100°C over 1 hour. Upon reaching 100°C, 5.44 g (0.0891 mole) ethanolamine dissolved in 19.85 g water was added to the reaction mixture. The reaction was held at 100°C for 1

hour and then raised to 130°C over 1 hour and held for an additional 8 hours. Cooling provided a clear yellow solution. The dried polymer had an acid number of only about 25 mg KOH/g polymer, indicating substantially all maleimide repeat units in the polymer.

EXAMPLE 18

Into a high pressure reactor was added: 154.0 g (1.00 mole) p(IB-MAn), 9.02 g (0.140 mole) ethylamine (70%), 10.97 g (0.150 mole) butylamine and 316 g ethanol. The reaction was purged with N₂ gas and the temperature raised to 130°C over 2 hours and held for 3 hours. The reaction mixture was cooled to which was added 36.65 g (0.600 mole) of ethanolamine dissolved in 176 g of water. The reactor was gradually reheated to 130°C over 3 hours and held for 8 hours. A clear yellow solution provided a polymer having an acid number of about 65 mg KOH/g polymer.

EXAMPLE 19

Into a high pressure reactor was added: 100 g (0.500 mole) monoethyl half ester of p(IB-MAn), 24.40 g (0.399 mole) ethanolamine, 3.66 g (0.0500 mole) butylamine, 4.63 g (0.0250 mole) dodecylamine, 84 g water and 150 g ethanol. The reaction was purged with N₂ gas and the temperature raised to 130°C over 2 hours and held for 8 hours. Upon cooling the resultant product was a clear yellow solution. The dried polymer had an acid number of about 65 mg KOH/g polymer.

EXAMPLE 20

Into a high pressure reactor was added: 60.0 g (0.390 mole) p(IB-MAn) powder, 6.26 g (0.0972 mole) ethylamine (70%), 7.13 g (0.0975 mole) butylamine and 175 g ethanol. The reaction was purged with N₂ gas and the temperature raised to 130°C over 3 hours and held for 5 hours. The reaction mixture was cooled to 30°C and 11.91 g (0.195 mole) of ethanolamine dissolved in 20 g water and 30 g ethanol was added slowly to the reaction mixture. The reactor was gradually reheated to 130°C over 3 hours and held for 5 hours. Upon cooling the resultant product was a clear yellow solution. The dried polymer had an acid number of about 45 mg KOH/g polymer.

EXAMPLE 21

60 g (0.390 mole) of a p(isobutylene-co-maleic anhydride) prepolymer and 150 g of water was charged into a 1-liter pressure reactor and purged with nitrogen. The reactor was gradually heated to 100°C and held for 1-hour. Then the reactor was heated to 130°C over a 1-hour period while 22.13 g (0.362 mole) ethanolamine was gradually added to the reaction mixture. Upon reaching 130°C, the reaction mixture was held for 8 hours and cooled. The product was a slight hazy, orange solution. Analysis of the product showed the presence of both maleamic acid and maleimide repeat units, with a higher molar ratio of maleamic acid units as compared to similar products obtained in an ethanol/water solvent.

EXAMPLE 22Hair/Spray/Compositions Containing
the Polymers of Examples 1-10

Low VOC hair spray compositions containing 5% by weight of each of the polymers of Examples 1-10 are prepared in ethanol and, optionally a hydrocarbon system. The polymers are neutralized with organic amines. Typical formulations thus contained 65% ethanol, 15% hydrocarbon, 15% water and 5% polymer (80% VOC); or 55% ethanol, 40% water and 5% polymer (50% VOC). The observed high humidity curl retentions for these systems were excellent.

EXAMPLE 22A

The polymers of the invention is formulated into a hydroalcoholic pump hair spray system containing as little as 3.5% water and a maximum of 91% water (VOC 4-92%).

Formula I

SD Alcohol 40B 200, Anhydrous	87.50%
Deionized Water	0.00
Imidized IB/MA Copolymer	12.50
(40% solids, 27% H ₂ O, 33% EtOH)	

Formula II

SD Alcohol 40B 200, Anhydrous	0.00%
Deionized Water	87.50
Imidized IB/MA Copolymer	12.50
(40% solids, 27% H ₂ O, 33% EtOH)	

EXAMPLE 22B

The polymers of the invention is formulated into a single phase hydroalcoholic aerosol hair spray system having a VOC content of 35% to 95%, with dimethyl ether as the propellant.

Formula III

SD Alcohol 40B 200, Anhydrous	52.50%
Deionized Water	0.00
Imidized IB/MA Copolymer	12.50
(40% solids, 27% H ₂ O, 33% EtOH)	
Dimethyl Ether	35.00

Resin solids 5%

Formula IV

SD Alcohol 40B 200, Anhydrous	0.00%
Deionized Water	52.50
Imidized IB/MA Copolymer	12.50
(40% solids, 27% H ₂ O, 33% EtOH)	
Dimethyl Ether	35.00

Resin solids 5%

Formula V

SD Alcohol 40B 200, Anhydrous	15.88%
Deionized Water	35.92
Imidized IB/MA Copolymer	12.50
(40% solids, 27% H ₂ O, 33% EtOH)	
Ammonium Hydroxide	0.30
MEA Borate (and) MIPA Borate	0.40
Dimethyl Ether	35.00
Resin solids 5%	
(Corrosion resistant in unlined tinsplate cans)	

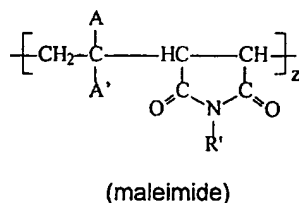
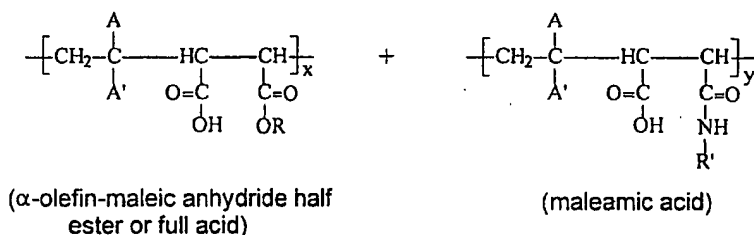
Formula VI

SD Alcohol 40B 200, Anhydrous	15.88%
Deionized Water	35.92
Imidized IB/MA Copolymer	12.50
(40% solids, 27% H ₂ O, 33% EtOH)	
Ammonium Hydroxide	0.15
Dimethyl Oxazolidine	0.15
MEA (and) MIPA Borate	0.40
Dimethyl Ether	35.00
Resin solids 5%	

The Formulas I-VI above also provide stiff feel on the hair at 5% resin solids comparable to an 80% VOC maximum hold, obtained with conventional retail hair sprays. In addition, advantageous humidity resistance (95% curl retention after exposure to 90% relative humidity, 80°F for 4 hours) is achieved in these 55% VOC hair sprays.

WHAT IS CLAIMED IS:

1. A derivatized polymer which contains repeat units of an α -olefin-maleic anhydride alkyl half-ester or full acid, and optionally, maleamic acid and/or maleimide repeat units, having the formula:



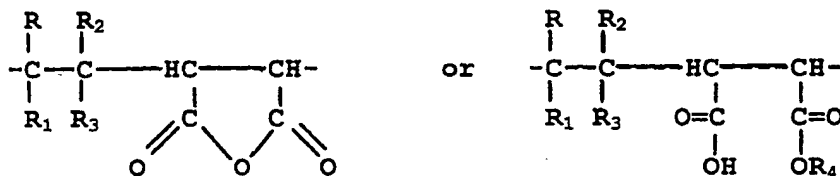
where A is independently H or C₁-C₄ alkyl;

R is H or C₁-C₄ alkyl, and R' is an α -unsubstituted primary amine; or hydroxy-containing α -unsubstituted primary amine having one or more of the following groups therein: hydrogen, silyl, amino, olefinic, carboxy and halogen; and

x is 0.01-1; y is 0-0.95; and z is 0-99.

2. A polymer according to claim 1 wherein R is ethyl.
3. A polymer according to claim 1 wherein A and A' = H.
4. A polymer according to claim 1 wherein A = H and A' = CH₃.
5. A polymer according to claim 1 wherein A and A' = CH₃.
6. A personal care product which includes the polymer of claim 1.
7. A hair spray composition which includes the polymer of claim 1 as fixative therein.
8. A hair spray composition according to claim 6 in a pump or aerosol formulation.
9. A hair spray composition according to claim 8 in which the polymer is present in a hair gel or mousse formulation.
10. A shampoo or hair conditioner product which includes the polymer of claim 1.
11. A skin care product which includes the polymer of claim 1.

12. A process of making the polymer of claim 1 which comprises reacting:



in aqueous or aqueous-alcoholic solution, where R, R₁, R₂, R₃ and R₄ are as defined above, with an α -unsubstituted primary amine, RNH₂, such as n-hexylamine, n-octylamine or 2-ethylhexylamine, or a hydroxy-containing α -unsubstituted primary amine, R'NH₂, where R' is as defined above, at a temperature of about 60°-160°C, for a reaction period of about 1-25 hours.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/09430

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C07D 207/40; A61K 7/06, 31/74

US CL :548/545; 424/70.1, 70.11, 70.12, 70.122, 78.2,

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 548/545; 424/70.1, 70.11, 70.12, 70.122, 78.2,

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A, P	US 5,886,194 A (ULMER ET AL.) 23 MARCH 1999	1-12



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*g* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

02 JUNE 1999

Date of mailing of the international search report

07 JUL 1999

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/09430

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/09430

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group 1, claim(s) 1-5 and 12, drawn to derivatized polymers and process of making said polymers. These are classifiable in class 548, subclass 545.

Group 2, claim(s) 6-11, drawn to personal care products. These are classifiable in class 424, subclass 70.1

The inventions listed as Groups 1 and 2 do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: this application contains inventions which are not so linked as to form a single inventive concept. The core structure is known as evidenced by EP 462469 A1. Therefore, the substituents provide special technical features to Group 1. Group 2 is drawn to personal care products such as evidenced in U.S. Patent no. 4,810,490. However, the composition of said product(s) may vary. Accordingly, unity of invention is considered to be lacking between the groups outlined above.